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Short communication

A general approach toward enhancement of pseudocapacitive performance of conducting polymers by redox-active electrolytes

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HIGHLIGHTS

- A general approach toward enhancement of conducting polymer pseudocapacitance by redox-active electrolytes is presented.
- The capacitance of the conducting polymer pseudocapacitors increase significantly by the redox-active electrolytes.
- The ionic conductivity of the redox-active electrolytes improved remarkably.

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ABSTRACT

A general approach is demonstrated where the pseudocapacitive performance of different conducting polymers is enhanced in redox-active electrolytes. The concept is demonstrated using several electroactive conducting polymers, including polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene). As compared to conventional electrolytes, the redox-active electrolytes, prepared by simply adding a redox mediator to the conventional electrolyte, can significantly improve the energy storage capacity of pseudocapacitors with different conducting polymers. The results show that the specific capacitance of conducting polymer based pseudocapacitors can be increased by a factor of two by utilization of the redox-active electrolytes. In fact, this approach gives some of the highest reported specific capacitance values for electroactive conducting polymers. Moreover, our findings present a general and effective approach for the enhancement of energy storage performance of pseudocapacitors using a variety of polymeric electrode materials.

1. Introduction

Electrochemical supercapacitors are considered excellent energy storage devices that can be found in many practical applications from consumer electronics and backup power systems to hybrid vehicles. [1–4] Supercapacitors can be basically divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors according to their different energy storage mechanisms. [5,6] Pseudocapacitive materials (such as metal oxides and conducting polymers) showed much higher capacitance than that of carbon based materials for EDLC due to their fast and reversible redox reactions. [7,8] Among them, conducting polymers are very promising materials for pseudocapacitors due to their low-cost, good electrochemical response, and high theoretical capacitances. [9–11] However, the obtained capacitance of conducting polymers is strictly limited by the available reactions between the electrode materials and electrolytes. [12] Different approaches have been adopted to improve the capacitance by electrode materials optimization. [13–15] However, further improvement of the capacitance has been extremely difficult due to the intrinsic limitation of the electrode materials that used in the supercapacitors. Therefore, attention should be paid to other components that make up the pseudocapacitors such as the electrolyte. Recently, Roldan et al. showed the greatly increased capacitance of carbon based supercapacitors by using a redox-active electrolyte. [16] However, the capacitance is still limited by the dominant double layer energy storage mechanism in the carbon based supercapacitors. To the best of our knowledge, there is no study of redox electrolyte being used in pseudocapacitors based on different conducting polymers.

In this study, we report for the first time the significant improvement of the pseudocapacitance through the application of redox-active electrolytes in pseudocapacitors employing various types of polymeric electrodes, including polyaniline (PAni), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT).

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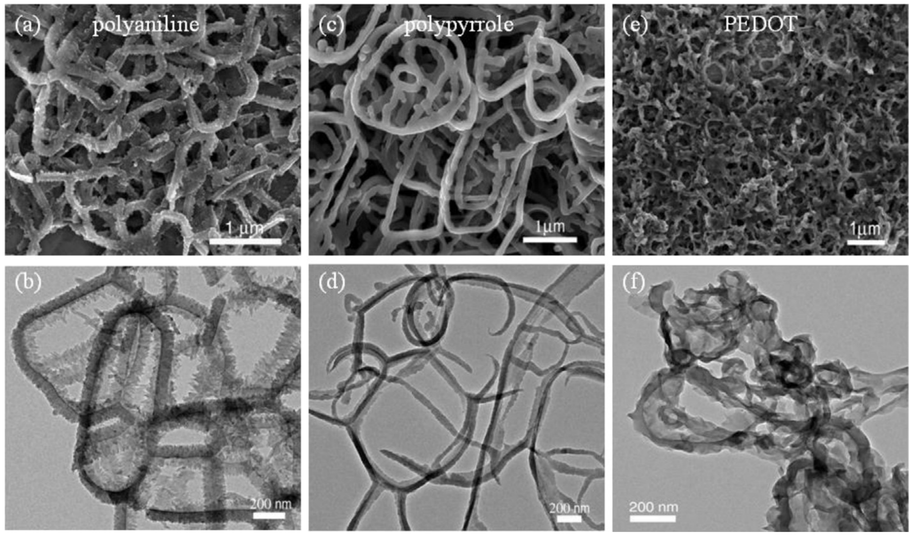

Fig. 1. SEM and TEM images of the three different conducting polymer nanofibers (a, b) polyaniline, (c, d) polypyrrole and (e, f) poly(3,4-ethylenedioxythiophene).

2. Experimental

2.1. Synthesis of conducting polymer nanofibers

The preparation of the three conducting polymer nanofibers (PAni, PPy and PEDOT) was followed by a modified oxidative template method that reported elsewhere. [17] Specifically, 0.01 M cetrimonium bromide (CTAB) was dispersed in 300 mL of 1 M HCl under stirring for 10 min in ice bath, followed by adding 0.03 M ammonium peroxydisulfate (APS) and stirring for another 10 min. 0.1 M conducting monomers (aniline, pyrrole and EDOT) were added separately into the prepared solution and the reactions were allowed to last for 24 h. The resulting products were washed with 1 M HCl, followed by water and ethanol repeatedly and freeze dried for 24 h.

2.2. Material characterization

The materials were characterized by scanning electron microscopy (SEM, Nova Nano 630, FEI), and transmission electron microscopy (TEM, Titan 80–300 kV (CT), FEI).

2.3. Electrochemical measurement

All electrochemical tests were conducted at room temperature in a classical two-electrode configuration. Conducting polymers acting as active materials were each mixed with acetylene black and polytetrafluoroethylene binder with a ratio of 80:10:10 in ethanol to form homogenous slurry. The electrodes were prepared by drop casting of the slurry onto graphitized carbon papers. Then the electrodes were vacuum dried at 60 °C for 12 h. The mass of the materials on the electrode was determined by a microbalance (Mettler Toledo XP26, resolution of 1 μg). The typical mass loading of the active materials is 3–4 mg cm^{-2}. The electrolytes used in this study are 1 M H_2SO_4 and 1 M H_2SO_4 with addition of different amount of hydroquinone (HQ). The electrochemical performance was measured in a VMP3 multi-channel electrochemical workstation (Bio-Logic) by the techniques of electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge–discharge (CD). The EIS was measured in the frequency range between 100 kHz and 100 mHz. The CV tests were performed from 5 mV s^{-1} to 100 mV s^{-1}, and the CD tests from 1 A g^{-1} to 30 A g^{-1} with voltage range between 0 and 0.7 V.

3. Results and discussion

Three different conducting polymer nanofibers (*i.e.* PAni, PPy and PEDOT) were prepared by a facile oxidative template based on a chemical polymerization process. [17] These three conducting polymers are among the most heavily investigated polymers for supercapacitor energy storage application due to their relatively high capacity, good electrical conductivity and excellent electrochemical behaviors. [10,18–20] As shown in Fig. 1, the as-obtained conducting polymers have a fiber-like morphology with different features. Specifically, the PAni nanofibers formed interconnected networks (Fig. 1a) and each nanofiber is found to be rough on its surface, making highly porous, caterpillar-like nanofibers (Fig. 1b). The average diameter of the PAni nanofibers is about 150 nm. In contrast, the PPy nanofibers have rather smooth surface and their diameters are between 60 nm and 120 nm (Fig. 1c and d). In the case of PEDOT, a porous film with inter-tangled nanofibers is formed (Fig. 1e). The curled worm-like nanofibers have an average diameter of 80 nm (Fig. 1f). The conducting polymer nanofibers with porous network features are believed to contribute to the high conductivity and easy access of electrolyte for high performance pseudocapacitors.

Fig. 2 shows the electrochemical performance of PAni nanofibers as pseudocapacitor electrode materials in conventional H_2SO_4 and redox-active electrolytes (H_2SO_4 + HQ) with different concentrations of HQ. It is shown that the PAni nanofibers in H_2SO_4 electrolyte exhibits the typical electrochemical behavior of PAni with a pair of redox peaks appears in the CV curve, corresponding to the Faradaic transformation of the emeraldine-pernigranilin form of PAni (Fig. 2a). [21] Once a small amount of HQ was added to the H_2SO_4 electrolyte (H_2SO_4 + 0.1 M HQ), the CV curve of PAni nanofibers deviates from quasi-rectangular shape and the redox peaks become shaper, indicating that extensive redox reactions are taking place in the pseudocapacitors that are caused by the redox electrolyte. The intensity of the redox peaks in CV curves at the same scan rate of 10 mV s^{-1} becomes larger with increasing HQ concentration in the redox electrolytes (Fig. 2a), resulting in the increased areas of the CV curves and thus the improved energy storage capacity. The CD curves show longer charge–discharge

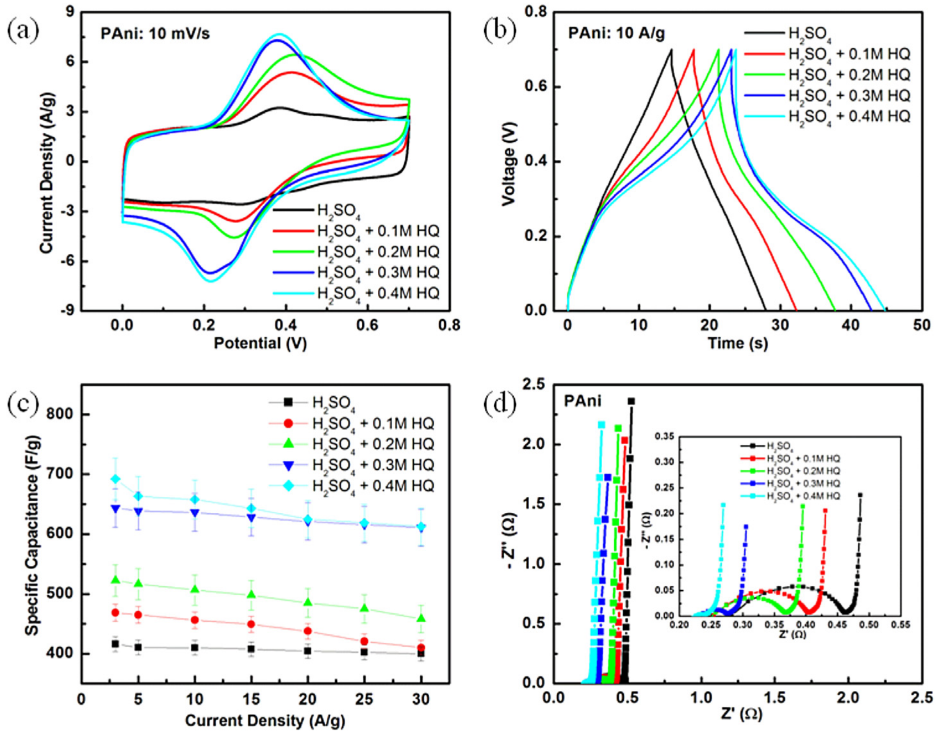

Fig. 2. Electrochemical performance of the polyaniline nanofibers as pseudocapacitor electrode materials in the redox-active electrolytes. (a) Cyclic voltammetry curves; (b) Galvanostatic charge–discharge curves; (c) specific capacitance vs. current density; (d) electrochemical impedance spectroscopy.

periods with increasing concentration of the redox electrolytes at the same current density of 10 A g^{-1} (Fig. 2b), consistent with the electrochemical behavior of the CV curves, indicating higher capacitance values.

Fig. 2c summarizes the values of specific capacitance change with current density for PAni pseudocapacitors in H_2SO_4 and H_2SO_4 + HQ electrolytes. It is clear that the specific capacitance of PAni pseudocapacitors in the redox-active H_2SO_4 + HQ electrolytes are much higher than that in conventional H_2SO_4 electrolyte. The capacitance values increase with the concentration of HQ in the H_2SO_4 + HQ redox electrolytes, confirming the electrochemical behavior observed from the CV and CD curves. The specific capacitance of 692 F g^{-1} at 3 A g^{-1} obtained by PAni pseudocapacitor in H_2SO_4 + 0.4 M HQ electrolyte is one of the highest values reported so far for PAni based full cell devices under relatively high mass loading of the active materials. [22] This value is much higher than 415 F g^{-1} at 3 A g^{-1} in the conventional H_2SO_4 electrolyte. As a fair comparison between the redox-active electrolyte and the conventional electrolyte, the capacitance values of conducting polymer pseudocapacitors in redox-active electrolytes are also calculated by subtracting the contribution from the redox-active agent according to the following equation:

$$C_{s(H_2SO_4)} = C_{s(H_2SO_4+HQ)} - C_{s(HQ)} \times HQ\% \big/ H_2SO_4\%$$

where $C_{s(H_2SO_4)}$, $C_{s(H_2SO_4+HQ)}$ and $C_{s(HQ)}$ are the specific capacitance from the part of H_2SO_4 that deducted the contribution from HQ, overall specific capacitance from the redox-active electrolyte, and the specific capacitance from HQ respectively. HQ% and H_2SO_4% are the percentages of HQ and H_2SO_4 in H_2SO_4 + HQ electrolytes.

Take the redox-active electrolytes of 1 M H_2SO_4 + 0.1 M HQ and 1 M H_2SO_4 + 0.4 M HQ in PAni pseudocapacitors as examples, the calculated specific capacitance from the H_2SO_4 after deducting the contribution from HQ are 480 F g^{-1} and 733 F g^{-1} at current density of 10 A g^{-1} respectively, which are substantially higher than the values obtained from the conventional 1 M H_2SO_4 electrolyte (410 F g^{-1}). This further indicates the effect of the redox-active electrolytes on improving the pseudocapacitance of the conducting polymers.

The PAni pseudocapacitors in the redox-active electrolytes show rate capabilities not as good as that in the conventional electrolyte (Fig. 2c), probably due to the different kinetics of the reactions that the redox-active electrolytes have with the electrodes under different current densities. At low current densities, the electrodes gain enough time to be fully charged and discharged in the redox-active electrolytes, where the intensive redox reactions contribute to the improved capacitance. While at high current densities, the electrodes have less time to react with the redox-active electrolytes, where the redox peaks that caused by the redox-active agents (HQ) cannot be completely formed, resulting in lower capacitance and thus lower rate capabilities.

Fig. 2d shows the evolution of the impedance with different electrolytes in PAni pseudocapacitors. The Nyquist plots of PAni show excellent electrochemical behaviors with very small impedance at high frequency range and nearly perfect electrochemical response in the low frequency range. [23,24] The overall resistance of the PAni pseudocapacitors decreases with the increase of HQ concentration in H_2SO_4 + HQ electrolytes, indicating the increased ionic conductivity of the electrolytes, which can be identified from the smaller solution resistances of the PAni pseudocapacitors in the redox-active H_2SO_4 + HQ electrolytes (the intersection of the EIS curves with the abscissa in Fig. 2d). Meanwhile, the redox-active H_2SO_4 + HQ electrolytes reduce the charge-transfer resistances of the pseudocapacitors, which are also revealed by the decreased semicircle arcs of the EIS curves at high frequency range. Due to the reactive agents produced by HQ from the redox-active electrolyte, the ionic conductivity of the electrolyte as well as the interface

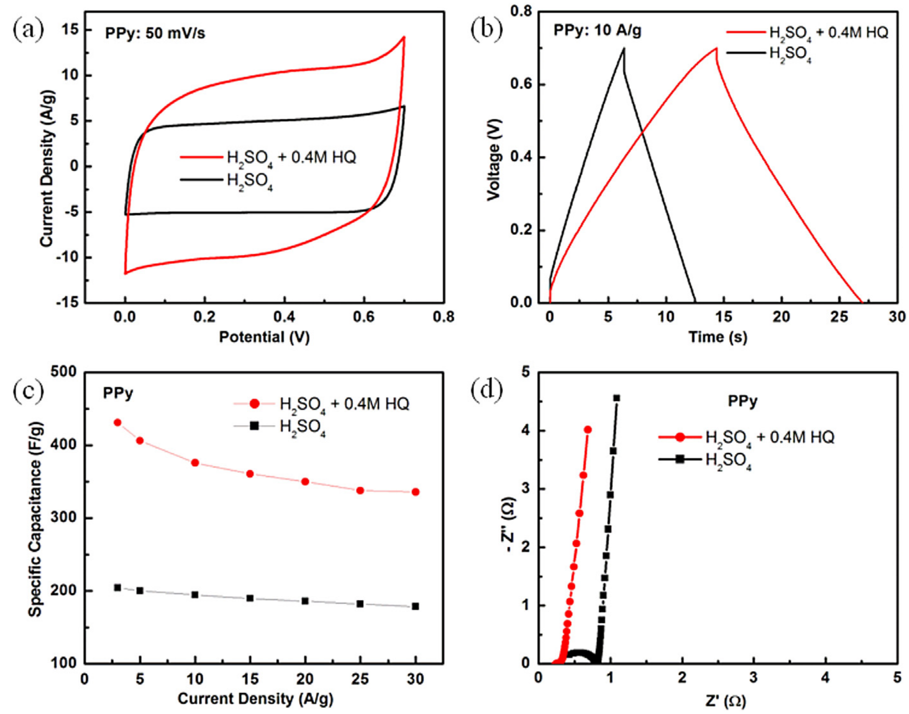

Fig. 3. Electrochemical performance of the polypyrrole nanofibers pseudocapacitors in conventional (H_2SO_4) and redox-active electrolytes (H_2SO_4 + 0.4 M HQ). (a) Cyclic voltammetry curves; (b) Galvanostatic charge–discharge curves; (c) Specific capacitance vs. current density; (d) Electrochemical impedance spectroscopy.

reaction between electrode and electrolyte increased accordingly, resulting in smaller electrode resistance in the redox-active electrolytes. The much improved capacitance and ionic conductivity of the electrolyte by the application of the redox-active mediator shows a very simple yet effective approach to achieve pseudocapacitors with better electrochemical performance.

To show that this approach is not specific to PAni and that it can be more generally applied to other materials, the H_2SO_4 + HQ redox electrolyte was adopted with two other conducting polymers, namely, PPy and PEDOT. Fig. 3 shows the electrochemical performance of the PPy pseudocapacitors in H_2SO_4 and H_2SO_4 + 0.4 M HQ redox electrolytes. The CV curve of PPy in H_2SO_4 electrolyte shows rectangular shape, suggesting its excellent electrochemical behavior as supercapacitor electrode material. The CV curve retained good rectangular shape when using the redox electrolyte in the PPy pseudocapacitors. However, the integrated area in the case of redox electrolyte has been significantly increased as compared to the use of conventional H_2SO_4 electrolyte at the same scan rate (Fig. 3a). This observation is supported by the longer charge and discharge duration time in H_2SO_4 + 0.4 M HQ redox electrolytes as compared to H_2SO_4 electrolyte from CD curve under the same current density (Fig. 3b). These results are summarized in Fig. 3c, which shows that the specific capacitance of PPy device is doubled in the redox electrolyte (431 F g^{-1} at 3 A g^{-1}) as compared to that in the conventional electrolyte (204 F g^{-1} at 3 A g^{-1}). Even at high current density of 30 A g^{-1}, the capacitance of PPy in the redox electrolyte is still as high as 336 F g^{-1}, much higher than that in conventional electrolyte (178 F g^{-1}). The very high specific capacitance of 431 F g^{-1} at 3 A g^{-1} is one of the highest reported values for PPy base pseudocapacitor full cells. [10,14] Moreover, the much better impedance behavior of PPy in the redox electrolyte compared to conventional electrolyte can be ascribed to the improved ionic conductivity by the application of redox electrolyte (Fig. 3d).

In the case of PEDOT pseudocapacitors, one can similarly see that the pseudocapacitive energy storage performance has also improved dramatically by using the redox-active electrolyte. It is shown that the integrated area of the PEDOT pseudocapacitors in the redox electrolyte is much higher than that in the conventional electrolyte (Fig. 4a), and the charge and discharge time is longer in the redox electrolyte (Fig. 4b). These results all indicate that a higher capacitance is obtained in the redox-active electrolyte compared to the conventional electrolyte (Fig. 4c). In fact, the capacitance is doubled when using the redox electrolyte in PEDOT-based pseudocapacitors (130 F g^{-1} in the redox-active electrolyte vs. 61 F g^{-1} in the conventional electrolyte at current density of 3 A g^{-1}). It is further demonstrated that the conductivity of the device is enhanced in the redox electrolyte as revealed by the impedance spectroscopy (Fig. 4d).

As an important parameter to reflect the energy storage performance, the long-term cycling stability of the three different conducting polymers based pseudocapacitors in conventional (H_2SO_4) and redox-active electrolytes (H_2SO_4 + HQ) were investigated and shown in Fig. 5. It is noticed that the cycling stability of the conducting polymer based pseudocapacitors in the redox-active electrolytes is not as good as that in the conventional electrolyte, which is due to the intensive redox reactions introduced by the redox-active electrolytes. As shown in Fig. 5a, the PAni pseudocapacitors retained 52%–65% of the initial capacitance after 10,000 cycles in the redox-active electrolytes, which is slightly lower than the retention in the conventional electrolyte (69%). However, due to the significantly improved capacitance of PAni pseudocapacitors in the redox-active electrolytes, the actual specific capacitance values in the redox-active electrolytes (285 F g^{-1}–342 F g^{-1} correspond to different concentrations) are still higher than that in the conventional electrolyte (283 F g^{-1}) even after 10000 cycles (Fig. 5b). Similarly, the retained specific capacitance of PPy pseudocapacitor in redox-active electrolyte (1 M H_2SO_4 + 0.4 M HQ) after 10000 cycles (184 F g^{-1}) is higher than that in the conventional H_2SO_4 electrolyte (170 F g^{-1}), and the value of PEDOT pseudocapacitor in redox-active electrolyte (1 M H_2SO_4 + 0.4 M

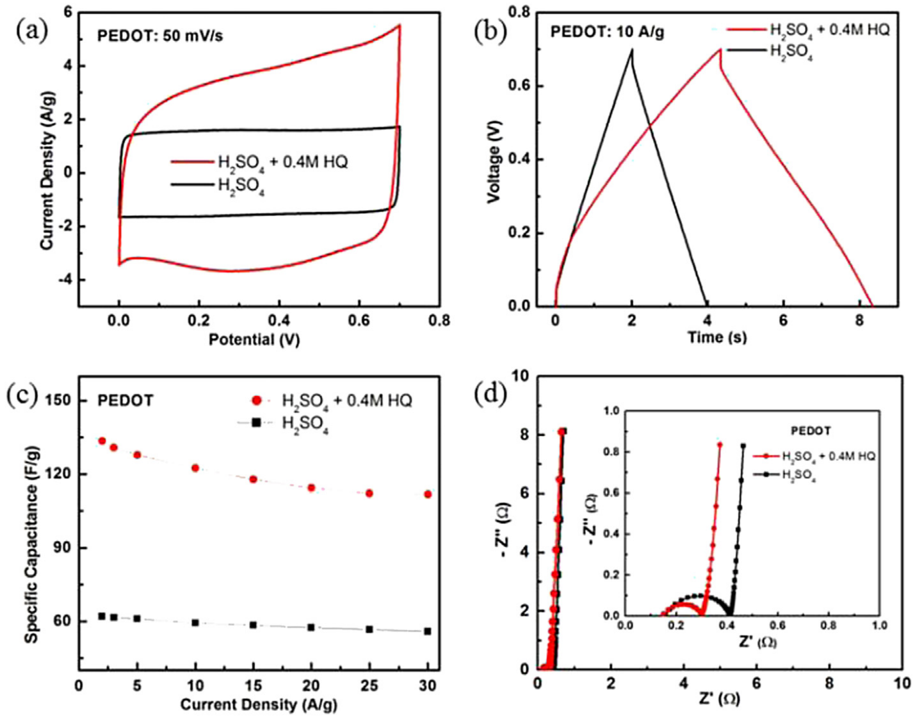

Fig. 4. Electrochemical performance of the PEDOT nanofibers pseudocapacitors in conventional (H_2SO_4) and redox-active electrolytes (H_2SO_4 + 0.4 M HQ). (a) Cyclic voltammetry curves; (b) Galvanostatic charge–discharge curves; (c) Specific capacitance vs. current density; (d) Electrochemical impedance spectroscopy.

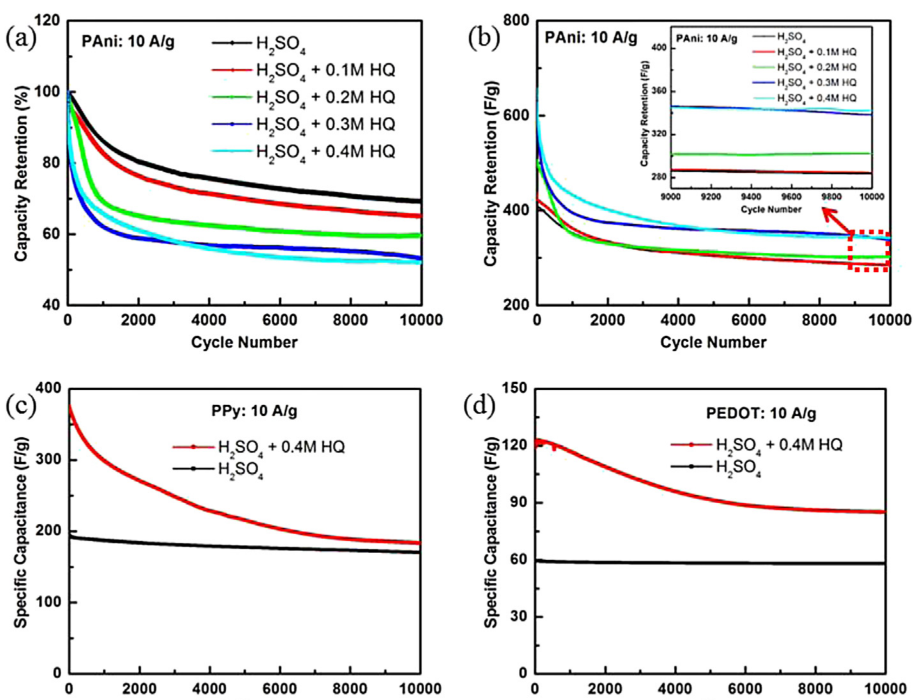

Fig. 5. Cycling stability of the conducting polymer based pseudocapacitors in conventional (H_2SO_4) and redox-active electrolytes (H_2SO_4 + HQ).

HQ) after 10000 cycles (85 F g^{-1}) is much higher than that in the conventional H_2SO_4 electrolyte (58 F g^{-1}), as shown in Fig. 5c and d respectively.

The energy storage mechanism of the conducting polymer based pseudocapacitors in redox-active electrolytes (H_2SO_4 + HQ) can be explained from the following two aspects. First, in addition to the redox reactions of the polymer that react with conventional part of the electrolyte (H_2SO_4), the redox-active agents (HQ) bring extra and intensive reactions to the electrodes, which together contribute to much increased pseudocapacitance. The faradaic reactions of the hydroquinone-quinone couples (HQ $= 2H^+ + Q^{2-}$) can easily produce a large amount of reactive ions (H^+) in the liquid

electrolytes, which will react with the polymer electrodes in additional sites and boost the overall capacitance. Second, the improved cell conductivity due to the increased ionic conductivity of the electrolyte (i.e., decreased solution resistance) and the decreased charge-transfer resistance make the electron transportation and ion diffusion much faster and more effective in the pseudocapaictors. The application of the redox-active electrolytes will greatly improve the energy storage capacity of the devices.

4. Conclusions

In summary, we demonstrate for the first time the successful application of redox-active electrolytes in pseudocapacitors using various conducting polymers. This general approach was demonstrated for polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) as pseudocapacitor electrode materials. The ionic conductivity of the electrolyte and the specific capacitance of the devices were significantly improved by incorporating the redox-active electrolytes. Furthermore, this approach gives some of the highest reported specific capacitance values for electroactive conducting polymers as pseudocapacitor electrode materials.

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